PAT-NO: JP02000212747A

DOCUMENT-IDENTIFIER: JP 2000212747 A

TITLE: SILICON NITRIDE THIN FILM AND ITS PRODUCTION

PUBN-DATE: August 2, 2000

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APPL-NO: JP11011841

APPL-DATE: January 20, 1999

INT-CL (IPC): C23C016/34

ABSTRACT:

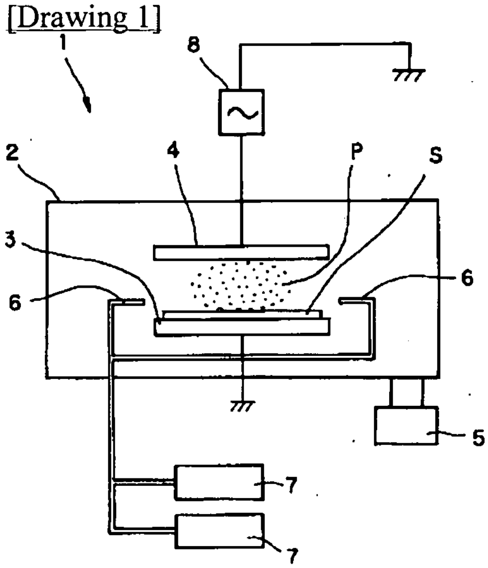
PROBLEM TO BE SOLVED: To give good transparency, high heat resistant adhesion property, shock-resistant adhesion property and excellent durability by forming a thin film consisting of silicon nitride on a substrate by using a silazane compd. by a chemical gas phase vapor deposition method.

SOLUTION: A substrate S is mounted on a lower electrode 3 in a plasma chemical gas phase vapor deposition device 1, and the chamber 2 is evacuated by a vacuum pump 5 to about ≤0.1 mTorr vacuum degree in the chamber. Then a gaseous silazane compd. (such as hexamethyldisilazane) and nitrogen gas supplied from a source material supply device 7 are mixed and introduced through a source material supply nozzle 6 into the chamber 2 to control the

pressure in the chamber 2 to about 10 to 200 mTorr. Specified high frequency voltage is applied from a power supply 8 to an upper electrode 4 to produce glow discharge plasma P near the opening of the source supply nozzle 6 and between the lower electrode 3 and the upper electrode in the chamber 2. A silicon nitride thin film is formed on the substrate S by the glow discharge plasma P.

DRAWINGS

[Drawing 1]



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* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the silicon nitride thin film excellent in the transparency used for hard coating, such as a silicon nitride thin film especially an insulating film, an acid-resisting film, a building material, and a car, etc., endurance, and insulation, and its manufacture approach.
[0002]
[Description of the Prior Art] It is used as insulating films, such as gate dielectric film and an interlayer insulation film, in the semi-conductor field, and also the silicon nitride thin film is used as hard coating, such as an acid-resisting film, a building material, and a car. For example, in addition to insulation, the insulating film used for the semi-conductor field requires endurance, such as acid resistance and thermal resistance.
[0003] as the above-mentioned silicon nitride thin film -- chemistry gaseous-phase vacuum evaporationo (CVD) -- the thin film which formed membranes on the base material by law, electron ray (EB) vacuum deposition, the sputtering method, the ion plating method, etc. is used.
[0004]
[Problem(s) to be Solved by the Invention] The silicon nitride thin film formed by the CVD method in the silicon nitride thin film formed by the above-mentioned various approaches is useful as a transparence thin film equipped with high endurance, even if thickness is small.
[0005] However, in membrane formation of the conventional silicon nitride thin film by the CVD method, when a membrane formation rate is raised (membrane formation time amount is short) or membranes are formed at low temperature, the endurance of a thin film becomes inadequate. Therefore, in order to obtain the silicon nitride thin film equipped with good endurance, the membrane formation rate needed to be made remarkably low (it is about membrane formation time amount), membranes needed to be formed at the elevated temperature (about 300 degrees C), and increase of a manufacturing cost was caused. Moreover, in membrane formation of the conventional silicon nitride thin film by the CVD method, in order to use gas with ignition qualities, such as silane gas, the danger on work environment became a problem, and offgas treatment equipment and a safety practice are required, and had become a manufacture top problem.
[0006] This invention is made in view of the above situations, and aims at offering the silicon nitride thin film which is excellent in endurance, such as abrasion resistance, thermal resistance, shock resistance, and corrosion resistance, insulation, and transparency, and its manufacture approach.
[0007]
[Means for Solving the Problem] in order to attain such a purpose -- the silicon nitride thin film of this invention -- a base material top -- a silazane compound -- using -- chemistry gaseous-phase vacuum evaporationo (CVD) -- it considered as a configuration which is the thin film which consists of silicon nitride which formed membranes by law.
[0008] moreover, the manufacture approach of the silicon nitride thin film of this invention -- chemistry

gaseous-phase vacuum evaporationo (CVD) -- it is the approach of forming a silicon nitride thin film on a base material by law, and considered as a configuration which uses a silazane compound as material gas.
[0009] By such this invention, handling is easy, and the formed silicon nitride thin film is precise, and it excels [the silazane compound of a raw material does not have explosivility, and] in endurance, insulation, and transparency, and very high adhesion is shown to a base material.
[0010]
[Embodiment of the Invention] Hereafter, this invention is explained with reference to a drawing. the silicon nitride thin film of this invention -- a base material top -- a silazane compound -- using -- chemistry gaseous-phase vacuum evaporationo (CVD) -- it is the thin film which consists of silicon nitride which formed membranes by law. As a silazane compound which is the raw material of a silicon nitride thin film, one sort, such as hexamethyldisilazane, tetramethyl disilazane, octamethyl TORISHIRAZAN, a hexa methyl SHIKUROTORI silazane, a tetraethyl tetramethyl SHIKUROTETORA silazane, and tetra-phenyl dimethyl disilazane, or two sorts or more can be used.
[0011] Although the thickness of the silicon nitride thin film of this invention changes with the purpose of using a silicon nitride thin film, the class of base material to be used, membrane formation conditions of a silicon nitride thin film, etc., it can be preferably made into about 100-10000A 50-20000A. If sufficient endurance cannot be acquired as thickness is less than 50A, and it exceeds 20000A, while the further improvement in endurance is not obtained, the time amount which membrane formation takes becomes long and is not desirable [improvement].
[0012] Heat-resistant adhesion with such a silicon nitride thin film very expensive to a base material good [transparency] and impact-proof adhesion are shown. Moreover, even if mechanical force external and a chemical act, it is hard to produce a crack, and a defect and the dissolution, and they can maintain the outstanding endurance (abrasion resistance, corrosion resistance, etc.) and the outstanding insulation [long duration].
[0013] The base material which forms the silicon nitride thin film of this invention can be suitably chosen from a transparent base material film, an electronic member, a structural member, the member for cars, etc. according to the purpose of using a silicon nitride thin film.
[0014] As a transparent base material film, for example Among these, polyethylene, polypropylene, Ethylene propylene rubber, polyolefine of Polly 4-methyl pentene-1 grade; Polyalkylene terephthalate, such as polyethylene terephthalate and polybutylene terephthalate, Polyester [, such as polyethylene -2 and 6-naphthalate,]; Polyamide; polyvinyl chloride; styrene system polymer; polyvinyl alcohol; polycarbonate; poly acrylic nitril, such as nylon 6, Nylon 11, Nylon 66, and Nylon 610; One sort, such as a cellulose system polymer Or the resin film which consists of two or more sorts of combination can be mentioned. As a desirable base material film, the base material film which consists of the olefin system polymer (especially polypropylene system polymer) which is excellent in transparency and a mechanical strength, polyester (especially polyethylene terephthalate, polyethylenenaphthalate), a polyamide (especially nylon 6), etc. can be mentioned especially.
[0015] As for the light transmission of the above-mentioned base material film, it is desirable that can choose suitably in the range which does not spoil visibility and the total light transmission in a white light line uses the base material film which is 70% or more more preferably 60% or more 40% or more. Moreover, a base material film may be a monolayer or a layered product. The thickness of a base material film can be suitably set up according to the purpose of use, for example, is about 3-100 micrometers.
[0016] The well-known shaping approaches, such as extrusion molding, can be used for shaping of a base material film, the base material film may not be extended, and although biaxial stretching may be carried out, uniaxial stretching or the biaxially oriented film which is excellent in a mechanical strength is more desirable.
[0017] Next, the manufacture approach of the silicon nitride thin film of this invention is explained. the manufacture approach of this invention -- a silazane compound -- using -- chemistry gaseous-phase vacuum evaporationo (CVD) -- a silicon nitride thin film is formed on a base material by law. chemistry

gaseous-phase vacuum evaporationo (CVD) -- as for law, plasma chemistry gaseous-phase vacuum deposition, thermochemistry gaseous-phase vacuum deposition, photochemistry gaseous-phase vacuum deposition, etc. are mentioned. For example, formation of the silicon nitride thin film to the base material top by plasma chemistry gaseous-phase vacuum deposition It introduces in a chamber by making the gas of a silazane compound, and nitrogen gas into material gas. To the electrode which maintained the pressure in a chamber to the pressure of 10 - 200mTorr extent, and was installed in the chamber, direct current voltage, Or the glow discharge plasma can be made to be able to generate by impressing alternating voltage, and a silicon nitride thin film can be formed on a base material by making material gas react with the activity of the plasma. Moreover, in photochemistry gaseous-phase vacuum deposition, by introducing material gas in the chamber maintained to the constant pressure, and irradiating laser light and ultraviolet radiation from the aperture of ****** attached in the chamber wall surface, energy can be made to be able to give and react to material gas, and, thereby, a silicon nitride thin film can be formed on a base material.
[0018] One sort of above-mentioned various silazane compounds or two sorts or more can be used for the silazane compound used by the manufacture approach of this invention.
[0019] Drawing 1 is drawing showing an example of the membrane formation equipment by plasma chemistry gaseous-phase vacuum deposition. In drawing 1 , parallel monotonous mold plasma-CVD equipment 1 is equipped with a chamber 2, the lower electrode (ground electrode) 3 arranged so that it might counter in this chamber 2, and the up electrode 4, and can set the inside of a chamber 2 now as a desired degree of vacuum with a vacuum pump 5. Furthermore, near the lower electrode 3 in a chamber 2 (ground electrode), opening (gas inlet) of the feeding nozzle 6 is located, and the other end of this feeding nozzle 6 is connected to the feeding equipments 7 and 7 currently arranged in the chamber 2 exterior. Moreover, it connects with a power source 8 and the up electrode 4 is promoting generating of the plasma.
[0020] A base material S is laid on the lower electrode (ground electrode) 3 of the above plasma-CVD equipments 1, the inside of a chamber 2 is decompressed with a vacuum pump 5, and a chamber degree of vacuum is set to 0.1 or less mTorrs. Then, the silazane compound and nitrogen gas which are supplied from the feeding equipments 7 and 7 and which were gasified are mixed, this mixed gas is introduced into a chamber 2 through the feeding nozzle 6, and the pressure in a chamber 2 is made into 10 - 200mTorr extent.
[0021] On the other hand, since predetermined high-frequency voltage is impressed to the up electrode 4 from the power source 8, the glow discharge plasma P is established between the lower electrode (ground electrode) 3 and the up electrode 4 (near the opening (gas inlet) of the feeding nozzle 6 in a chamber 2). A silicon nitride thin film is formed on a base material S by this glow discharge plasma P.
[0022] In addition, the membrane formation equipment by the plasma chemistry gaseous-phase vacuum deposition used by the manufacture approach of this invention may be a roll membrane formation machine which forms a silicon nitride thin film, not being limited to the parallel monotonous mold plasma-CVD equipment of an above-mentioned batch type, and making coating drum lifting convey the original fabric of a base material S within a chamber.
[0023]
[Example] Next, an example is given and this invention is further explained to a detail.
(Example) The silicon wafer and the biaxial-stretching polyethylene terephthalate (PET) film (Toray Industries, Inc. make T-60 (thickness of 100 micrometers)) were prepared as a base material, and it equipped with this on the lower electrode (ground electrode) in the chamber of parallel monotonous mold plasma-CVD equipment (PE401 made from Anelva). Next, the inside of the chamber of plasma-CVD equipment was decompressed to ultimate-vacuum 0.1mTorr with the oil sealed rotary pump and the oil diffusion pump.
[0024] Subsequently, the hexamethyldisilazane of a liquid was prepared as a silazane compound, and it evaporated with the carburetor heated at 100 degrees C, and considered as material gas, carrying out control of flow of this, and the chamber was supplied by the flow rate of 2sccm (gaseous state). Moreover, nitrogen gas was supplied to the chamber by the flow rate of 60sccm(s) as other material gas.

[0025] Next, by impressing power (200W and 13.56MHz) between an up electrode and a ground electrode, the plasma was generated, the pressure in the chamber at the time of membrane formation was maintained at 50mTorr(s), and membrane formation for 5 minutes was performed. In addition, water cooling of the base material at the time of membrane formation was carried out, and it was held to the room temperature. Consequently, the silicon nitride thin film with a thickness of about 1000A was formed on the base material.
[0026] (Example of a comparison) The silicon wafer was prepared as a base material and it equipped with this on the lower electrode (ground electrode) in the chamber of parallel monotonous mold plasma-CVD equipment (SLPC[by Shimadzu Corp.]- 68 H). Next, the inside of the chamber of plasma-CVD equipment was decompressed to ultimate-vacuum 0.1mTorr with the oil sealed rotary pump and the oil diffusion pump.
[0027] subsequently -- as material gas -- silane gas (SH4) -- nitrogen gas was supplied for ammonia to the chamber by the flow rate of 500sccm(s) with the flow rate of 60sccm(s) by the flow rate of 20sccm (s).
[0028] Next, by impressing power (200W and 13.56MHz) between an up electrode and a ground electrode, the plasma was generated, the pressure in the chamber at the time of membrane formation was maintained at 50mTorr(s), and membrane formation for 12 minutes was performed. In addition, the base material at the time of membrane formation was heated at 300 degrees C. Consequently, the silicon nitride thin film with a thickness of about 1000A was formed on the base material.
[0029] In addition, since silane gas (SH4) with an ignition quality was included, the exhaust gas of a chamber was processed using exhaust gas treatment equipment by incineration process. Moreover, the leak detector was installed in the installation of a chemical cylinder or equipment for the safety practice.
[0030] (Evaluation) About the silicon nitride thin film (an example, example of a comparison) produced as mentioned above, specific resistance was evaluated [abrasion resistance, adhesion, heat-resistant adhesion, impact-proof adhesion, corrosion resistance, light transmittance (example), and] as follows, it measured, and the result was shown in the following table 1.
[0031] Wear-resistant SPM by the evaluation U.S. DI company Equipped with the diamond coat probe by the nano sensor company, it measured by carrying out the configuration of friction marks after 100 times friction by the predetermined load at the super-light load to the silicon nitride thin film formed on the base material, and evaluation wear-resistant on the following criteria was performed to D3000.
(Valuation basis)
O: [0032] as which friction marks are regarded by x:silicon nitride thin film with which friction marks are not looked at by the silicon nitride thin film Tape exfoliation by the adhesion cross hatching method was performed, and five steps of the following criteria estimated adhesion with remaining extent of a hatch way.
(Valuation basis)
A: remainder 100 - 80%B: of a hatch way -- remainder 80 - 60%C: of a hatch way -- remainder 60 - 40%D: of a hatch way -- remainder 40 - 20%E: of a hatch way -- remainder 20 - 0% of a hatch way
[0033] To the silicon nitride thin film formed on the evaluation base material of heat-resistant adhesion, the 25-100-degree C temperature change (a temperature up, cooling) was given 10 times at the varying temparature rate for 15-degree-C/, tape exfoliation by the cross hatching method was performed like the evaluation approach of the above-mentioned adhesion after that, and five steps of criteria estimated adhesion.
[0034] Supersonic vibration (100W and 39kHz) was impressed to the silicon nitride thin film formed on the base material for 15 minutes using UTby evaluation Sharp Corp. 104 ultrasonic washer of impact-proof adhesion, tape exfoliation by the cross hatching method was performed like the evaluation approach of the above-mentioned adhesion after that, and five steps of criteria estimated adhesion.
[0035] 25 degrees C of solution temperature, the nitric acid of 30% of concentration, the hydrochloric acid, and the sulfuric acid were prepared as a corrosion-resistant evaluation acid, 1-N sodium-hydroxide solution of 25 degrees C of solution temperature was prepared as alkali, the erosion condition of the silicon nitride thin film after being immersed for 20 minutes into each liquid and pulling up a silicon

nitride thin film with a base material (silicon wafer) was observed, and the following criteria estimated. (Valuation basis)
O: [0036] as which erosion is regarded by x:silicon nitride thin film with which erosion is not seen by the silicon nitride thin film Permeability with a wavelength of 550nm was measured about the silicon nitride thin film formed on the measurement PET film of light transmittance.
[0037] The test piece of metal-insulator-semiconductor structure (nickel / silicon nitride thin film / P+-Si) was produced using the measurement silicon nitride thin film of specific resistance, a current potential property and capacity measurement were performed, and it asked for the specific resistance rho in 1 MV/cm (ohm-cm).
[0038]
[Table 1]

表 1

窒化珪素薄膜	耐摩耗性	密着性	耐熱密着性	耐衝撃密着性	耐蝕性	光透過率（%）	比抵抗 ρ（Ω・cm）
実施例	○	A	A	A	○	82	1.0×10^{10}
比較例	○	A	A	A	○	--	2.0×10^{10}

As shown in Table 1, endurance and insulation were high level like the conventional silicon nitride thin film (example of a comparison) produced using silane gas, and the transparency of insulation of the silicon nitride thin film (example) of this invention was also good. From this, although low-temperature membrane formation was possible for the silicon nitride thin film of this invention and the safety at the time of membrane formation was very high, having the extremely excellent property was checked.
[0039]
[Effect of the Invention] according to [as explained in full detail above] this invention -- a base material top -- a silazane compound -- using -- chemistry gaseous-phase vacuum evaporationo (CVD) -- the formed silicon nitride thin film, since membranes are formed by law and it considers as a silicon nitride thin film Transparency is good, and is precise and very high adhesion is shown in a base material. the endurance (abrasion resistance --) which neither a crack nor a defect arose but was excellent even if mechanical force external acted A long time is covered, insulation, such as heat-resistant adhesion, impact-proof adhesion, and corrosion resistance, can be maintained, and it can use for hard coating, such as an insulating film in the semi-conductor field, and an acid-resisting film, a building material, a car, etc. Moreover, explosivility does not have the silazane compound of a raw material, either, handling is easy, and since it is not necessary to use the high gas of danger at the time of membrane formation, there is also no problem in a safety aspect and low-temperature membrane formation can be performed further, thermal degradation is not given to a base material.

[Translation done.]